USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 507
DETERMINATION OF TRACE ELEMENTS BY ICP-MS

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1 SCOPE AND APPLICABILITY

This SOP provides procedures for the determination of dissolved and total recoverable elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) in environmental samples for use in the USEPA Region 9 Laboratory, Richmond, CA. It is applicable to ground, surface, drinking, and storm runoff water samples; industrial and domestic waste waters. Additionally, this SOP has been extended to the analysis of fish tissue. The procedures are based on EPA Method 200.8, *Determination of Trace Elements in Waters and Wastes by ICP – MS*, Rev. 5.4, May 1994. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

Water samples with turbidity >1 NTU or where silver and/or total recoverable analytes are requested must be digested following EPA Region 9 Laboratory SOP 403 prior to analysis. Other water samples (primarily drinking water, but may also be a project specific request) may be analyzed directly after proper filtration and/or acid-preservation. Fish tissue is prepared by microwave digestion following EPA Region 9 Laboratory SOP 420 prior to analysis.

2 METHOD SUMMARY

This SOP describes the determination of trace elements in aqueous samples by ICP-MS by direct analysis or after digestion with nitric and hydrochloric acids. Sample solutions are introduced by pneumatic nebulization into a plasma, in which desolvation, atomization, and ionization occurs. Ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadruple mass spectrometer. The ions transmitted through the quadruple are detected by an electron multiplier. Ion intensities at each mass are recorded and compared to those obtained from external calibration standards to generate concentration values for the samples. Results are corrected for instrument drift and matrix effects using internal standards. Additional corrections are applied as necessary to correct for isobaric and polyatomic elemental interferences.

The dynamic reaction cell (DRC) simultaneously employs two techniques for the elimination of interferences, chemical resolution, and dynamic bandpass tuning (DBT). Chemical resolution involves the use of a gas within the DRC cell, which reacts with the interference to eliminate it. The DBT is applied at the same time using a bandpass mass filter which provides a high mass cut off and a low mass cut off to define a precise bandpass window, thus preventing the formation of new species that may interfere with the analysis.

3 DEFINITIONS

Analytical Sample – Any sample introduced into the ICP-MS instrument, excluding calibration standards, blanks, or QC reference samples.

Calibration Blank (CB) – A blank that is the same matrix as the calibration standards, but without the analytes. The calibration blank is also a zero standard used to calibrate the ICP-MS instrument. The CB is also known as the initial calibration blank (ICB) and the continuing calibration blank (CCB).

Continuing Instrument Calibration Verification (CCV) – The CCV standard is the same solution as the ICV standard and is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at end of the analytical run). The CCV is also known as the continuing instrument performance check (IPC) standard.

Dissolved Analyte – The concentration of analyte in an aqueous sample that is filtered through a 0.45-µm membrane filter assembly prior to sample acidification.

Initial Calibration Standard (ICAL) – Standards used to calibrate the instrument response with respect to analyte concentration.

Initial Instrument Calibration Verification (ICV) – A standard containing the analytes of interest that is used to verify the accuracy of the analysis. It is analyzed immediately after calibration. The ICV is also known as the initial instrument performance check (IPC) standard.

Internal Standard – An element added to all sample, extract, and standard solutions in the same known amount. Its response is measured throughout an analytical run and is used to correct for instrument drift and sample transport interferences. The internal standard should not be a sample constituent. Recommended internal standard elements are listed in Appendix D, Table 1.

Laboratory Control Sample (LCS) – An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

Laboratory Information Management System (LIMS) – The Element Database.

Linear Dynamic Range (LDR) – The concentration range over which the instrument response to an analyte is linear. The LDR study is used to define the concentration of the highest calibration standard.

Matrix Spike (MS) – An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be

determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as a laboratory fortified matrix (LFM) sample.

Matrix Spike Duplicate (MSD) – A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MSD is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MSD corrected for background concentrations. The MSD is also known a laboratory fortified matrix duplicate (LFMD) sample.

Method Blank (MB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as a laboratory reagent blank (LRB).

Method Detection Limit (MDL) – The minimum concentration of an analyte in an environmental sample that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Quantitation Limit (QL) – The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) – A standard used to check the accuracy of the analysis at the quantitation limit.

Sample Delivery Group (SDG) – A group of samples, usually twenty or fewer, from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) – A solution of method analytes of known concentration that is prepared from a source different from the source of the calibration standards. (A different lot from the same source may be used for multiple component analytes if a suitable second source is not available). It is used to check the accuracy of the initial calibration solutions. The SCV is also known as a quality control standard (QCS).

Stock Standard Solution (SSS) – A concentrated standard containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Total Recoverable Analyte Concentration – The concentration of an analyte in an unfiltered aqueous sample after preparation by acid digestion.

Tuning Solution – A solution containing selected elements over the entire mass range of the method. It is used to tune the mass calibration and resolution of the mass spectrometer, and to assess instrument performance prior to calibration and sample analysis.

Water Sample – For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

The ICP-MS emits radio frequency and intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The instrument is shielded to minimize exposure to these hazards and the shields should always be in place during operation.

Always wear safety glasses for eye protection (and a full face shield if large quantities of concentrated acids are being transferred), protective clothing, and observe proper mixing when working with these reagents.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
ICP/MS instrument liquid waste (nitric acid, hydrochloric acid, trace metals)	Hazardous Waste	Corrosive, Toxic
Pump Oil	Hazardous Waste	Other

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 500 mL sample volume should be sufficient to meet these objectives.

Whole fish samples are usually received wrapped in aluminum foil. Other tissue samples should be collected in pre-cleaned glass or plastic (if only inorganic analyses are requested) jars. There should be sufficient sample to ensure a representative sample, allow for replicate analysis and minimize waste disposal. A 10 g sample should be sufficient to meet project requirements if the analytical scope is limited to metals.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

1. Dissolved Analyte Samples

   The samples must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid contamination. The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with dilute (1:1) nitric acid immediately following filtration to pH <2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient).

2. Drinking Water Samples

   Samples are preserved by acidifying with dilute nitric acid to pH <2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH <2 just prior to withdrawing an aliquot for turbidity measurement. If the sample turbidity is <1 NTU, the sample can be analyzed directly without digestion (i.e. low level analysis). If turbidity is >1 NTU, perform the acid digestion for total recoverable analysis.

3. Aqueous Total Recoverable Analyte Samples

   Samples are preserved by acidifying with dilute nitric acid to pH <2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH <2 just prior to withdrawing an aliquot for digestion or 'direct analysis'. If the pH of the sample is >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2.

5.4 Sample Storage

Aqueous samples must be stored at > 0 and $\leq$ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

Fish tissue sample must be received and stored at $\leq$ -20 °C. Any deviations from the $\leq$ -20 °C temperature requirements must be noted in the report narrative. Any samples received unfrozen must be frozen upon receipt.

5.5 Holding Time

Aqueous samples must be analyzed within six months from collection.

Recommended tissue sample holding times are analysis dependent and vary by agency. The table below reflects the guidelines in *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume 1 Fish Sampling and Analysis,"* Office of Water, Washington, DC, Third Edition, November 2000. The analyst must review the project specific requirements with regard to holding times.

Analyte	Holding time
Metals (excluding Hg)	6 months

6 INTERFERENCES

1. Isobaric Elemental Interferences

Isobaric elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and cannot be resolved with the instrument's spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the interfering element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

All analytes listed in Appendix B have at least one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only antimony-123 (tellurium), molybdenum-98 (ruthenium), and selenium-82 (krypton) have isobaric elemental interferences. (Refer to Appendix D, Table 3). If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. Such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

2. Abundance Sensitivity Interference

Abundance sensitivity interference refers to the degree of peak overlap that can occur between adjacent peaks. The interference can occur when the shoulder of a large peak

significantly overlaps the peak of a neighboring minor peak, thereby contributing to its intensity. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

3. Isobaric Polyatomic Ion Interferences

   Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and cannot be resolved by the instrument's spectrometer. Examples include $ArCl^+$ (mass 75), which interferes with As, and ClO^+ (mass 51) which interferes with V, which must be corrected by measuring ClO^+ at mass 53. This in turn must be adjusted for contribution from Cr at mass 53. These interferences are highly dependent on the matrix of the samples and day-to-day plasma conditions, so correction factors may be determined on the day of analysis. When possible, one should choose an interference-free isotope to measure.

   The Region 9 Laboratory does not routinely calculate these correction factors and uses the recommended elemental equations for data calculations that are listed in Appendix D, Table 2. Alternatively, the Dynamic Reaction Cell (DRC) uses chemical resolution to remove polyatomic interferences using reaction gasses. The reaction gas is chosen such that it reacts with the interfering species to form a new, non-interfering species of a different mass. The new species is then mass separated prior to entry into the analyzer and the interference is effectively removed. The DRC can also use a reaction gas to react with the analyte of interest to form a new molecular species that is then analyzed at a mass that is free of the interference. An example is arsenic in the presence of oxygen in the DRC mode to form arsenic oxide, which is analyze at mass 92, thus eliminating the $ArCl^+$ interference present at arsenic mass 75.

4. Physical Interferences

   Physical interferences result from the physical processes associated with the transport of sample to the plasma, sample behavior within the plasma, and transmission through the interface region between the plasma and the mass spectrometer. Viscosity and surface tension differences can affect results, as can deposits on the sample and skimmer cones caused by large quantities of dissolved solids in the samples. The interferences can be compensated for by the use of internal standards that approximate the analytical behavior of the elements being determined. Additionally, it is recommended that dissolved solids in samples be kept below 0.2% (w/v).

5. Memory Interferences

   Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are

dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

The rinse times necessary for a particular analyte should be estimated prior to analysis. This can be achieved by aspirating a standard containing the analyte at a concentration ten times the highest calibration standard for the normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce the analyte signal to less than ten times the method detection limit should be noted. The minimum rinse time between samples should be set to this time. Memory interferences may also be assessed within an analytical run by using three or more replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should check for the possibility of a memory effect. If the analyte concentration in the previous sample is high enough to suspect analyte carryover, the sample should be re-analyzed after a long rinse period.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Refer to EPA Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures*, for specific instructions.

7.1 Instruments and Equipment

- Perkin Elmer Elan DRC Plus Inductively Coupled Plasma Mass Spectrometer
  - Cetac Autosampler
  - Cetac Autodilutor
  - Gilson Minipuls3 Peristaltic Pump
  - Polyscience 6105 – Refrigerated Circulator

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use. Record all reagent preparations in the LIMS.

- Reagent Water – All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825.

- Hydrochloric Acid (HCl), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Hydrochloric Acid, dilute (1:1) – Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.
- Nitric Acid (HNO_3), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Nitric Acid, dilute (1:1) – Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1L.
- Argon gas supply, high-purity grade, 99.99%
- DRC Reaction gas – Ammonia, electronic grade, 99.99%
- DRC Reaction gas – Oxygen, research grade

7.3 Standards

Record all standards and standard preparations in the LIMS.

7.3.1 Stock Standards

Stock standard solutions are available from commercial suppliers such as Spex or Inorganic Ventures. Multi-element solutions containing elements listed in Appendix B are typically used.

7.3.2 Initial Calibration Standards

Prepare initial calibration standards at a minimum of three levels. Use multi-element stock solutions (Section 7.3.1) as the source and dilute to the appropriate volume with 1% (v/v) nitric acid.

For routine analysis, prepare standards to contain 10 µg/L and 20 µg/L for all elements; 100 µg/L for As, Se, Be, Al, V, Cr, Mn, Co, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th, and U; and 200 µg/L for Ni, Cu, and Zn.

For low level, direct analysis, prepare standards to contain element concentrations at 10 µg/L, 20 µg/L, and 50 µg/L for each element.

NOTE: High level standards may also be used for undiluted samples containing levels of analytes greater than 50 µg/L. Higher level standards may

also be used as an additional calibration point to expand the linear range if warranted by high level concentrations inherent in samples.

Prepare fresh calibration standards every two weeks or as needed.

7.3.3 ICV/CCV Standard

The ICV standard and CCV standard are identical and only differentiated by their place within the analytical sequence. For routine analysis, a 50 µg/L ICV/CCV is typically analyzed. For low level, direct analysis, a 20 µg/L is typically used. Prepare each solution as needed from multi-element stock solutions (Section 7.3.1) in 1% (v/v) nitric acid.

7.3.4 CB

Dilute concentrated nitric acid with reagent water to obtain a 1% (v/v) nitric acid solution.

7.3.5 MB

Prepare the MB using reagent water plus all of the reagents used in processing the samples. The MB is taken through the entire preparation and analytical sequence.

7.3.6 LCS and MS/MSD

Prepare the LCS by fortifying an aliquot of reagent water from multi-element stock solutions (Section 7.3.1). Process the LCS and MS/MSD through the entire preparation and analytical sequence.

For routine analysis, prepare the LCS by fortifying an aliquot of reagent water to contain 40 µg/L of each analyte except aluminum which should be fortified at 80 µg/L. Prepare the MS/MSD by fortifying an aliquot of the QC sample with the stock standards to contain 40 µg/L of each analyte except aluminum which should be fortified at 80 µg/L

For low level, direct analysis, prepare the LCS and MS/MSD concentrations to contain 25 µg/L of each analyte.

7.3.7 SCV

Prepare SCV standards in 1% (v/v) nitric acid from multi-element stock standards from a source different from the calibration standards.

For routine analysis, prepare a standard to contain 50 µg/L of each analyte.

For low level, direct analysis, prepare a standard to contain 20 µg/L of each analyte.

7.3.8 QLS

Prepare the QLS as needed from multi-element stock solutions (Section 7.3.1) in 1% (v/v) nitric acid as shown in the following table:

QLS Concentrations

Element	Routine Analysis, µg/L	Low-level, Direct Analysis, µg/L
Co Ag U	0.25 µg/L	0.125 µg/L
Cd	0.4 µg/L	0.2 µg/L
As Be Mo Sb	0.5 µg/L	0.25 µg/L
Ba Cr Pb Ni Se Tl Th	1 µg/L	0.5 µg/L
Cu Mn	2 µg/L	1 µg/L
V	4 µg/L	2 µg/L
Zn	5 µg/L	2.5 µg/L
Al	20 µg/L	10 µg/L

7.3.9 Rinse Blank

Dilute concentrated nitric acid with reagent water to obtain a 2% (v/v) nitric acid solution.

7.3.10 Internal Standard Solution

Prepare internal standards from single-element stock standards (Section 7.3.1) to contain 200 µg/L lithium6 and 100 µg/L each of gallium, holmium, indium, rhodium, scandium, terbium, and yttrium in 1% (v/v) nitric acid.

7.3.11 Tuning Solution

Prepare an intermediate standard to contain 1,000 µg/L of barium, beryllium, cerium, cobalt, indium, lead, magnesium, thorium, and uranium from single-element stock standards (Section 7.3.1). Prepare a working solution from the intermediate standard at 1.0 µg/L in 1% (v/v) nitric acid.

7.3.12 Dual Detector Cross Calibration Solution

The dual detector cross calibration solution is used to correlate the pulse and analog modes of the detector for extended linear ranges.

Prepare a solution of all available elements across the entire mass range using the multi-element standards (Section 7.3.1) in 1% (v/v) nitric acid at concentrations of 100 µg/L to 500 µg/L.

7.4 Supplies

- Auto-sampler tubes
- Automatic pipettes capable of delivering volumes of 10 to 1,000 µL
- Class A volumetric flasks, graduated cylinders, and funnels (glass and/or metal-free plastic)
- Class A volumetric pipettes
- Metal-free disposable tips
- Narrow-mouth storage bottles with screw closure, 125-mL to 1-L capacities
- Syringe with 0.45 µm disk filters
- Wash Bottle with screw closure, 500-mL to 1,000-mL capacity

8 ANALYTICAL PROCEDURES

It is recommended that samples with unknown or unusual history be screened by ICP for elements at high concentration. Alternatively, samples may be screened using a semi-quantitative ICP/MS analysis at a 500-fold dilution.

8.1 Instrument Operation

Set-up the ICP-MS following operating instructions provided by the manufacturer and discussed below. Use operating parameters provided in Appendix E as a starting point.

Ensure that all appropriate waste containers are properly connected and labeled.

Ignite the plasma and stabilize for at least 30 minutes. During this stabilization period, run the tuning solution (described in Section 7.3.11) using indium signal to align the torch.

Open a method that contains all necessary masses for the analytes of interest or open a master method and edit so that all masses which are necessary to perform elemental calculations (for interference corrections) and which can provide information concerning data quality are monitored during the analytical run. Refer to Appendix D,

Table 2 for required masses. Enter the daily data set file name (report file name) in the report tab and save the method. Create a new data set file and save workspace.

At a minimum, masses for the elements of interest prescribed in Appendix D, Table 3 must be monitored in the same scan used for the collection of the data. For elements run in DRC mode, interference corrections calculations are not necessary. Create a new data set file and save workspace.

Initialize the autosampler and create a sample table. If the autodiluter is to be used, initialize the autodiluter and edit the autosampler table as appropriate.

Ensure that all appropriate waste containers are properly connected and labeled.

8.1.1 Tuning and Mass Calibration

After the plasma system (i.e., torch box, plasma, and spray chamber) has stabilized, verify and adjust the mass calibration and resolution.

Check the spectrometer resolution with beryllium, magnesium, cobalt, indium, and lead. Also monitor argon dimmer, cerium, and thorium.

The resolution should produce a peak width of approximately 0.75 atomic mass unit (amu) at 5% peak height. For the PE Elan, the resolution of 0.625 to 0.675 at 10% peak height corresponds to approximately 0.70 to 0.75 amu peak width at 5% peak height.

Adjust the mass calibration to ensure 0.1 amu accuracy from unit mass.

8.1.2 Sensitivity and Stability Check

Analyze the tuning solution (Section 7.3.11) a minimum of five times for daily performance check. The RSD for each element must be less than 5% before the instrument can be calibrated and samples analyzed.

Instrument sensitivity should be, at a minimum, as listed below:
Mg – 6,000 counts per second (CPS)
In – 30,000 CPS
U – 20,000 CPS

To avoid interferences, it is preferable that oxide (Ce) and ++ (Ba) levels not exceed 3%. If they do, depending on the specific analysis to be performed, maintenance or instrument adjustments may be required before proceeding with the analysis.

8.2 Calibration and Standardization

8.2.1 Internal Standardization

Internal standards are used to correct for instrument drift and physical transport interferences. Internal standards are automatically added to all samples, standards, and blanks by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. For full mass range scans, a minimum of three internal standards must be monitored and used for calculation.

NOTE: The concentration of the internal standard should be sufficiently high that good measurement precision is obtained while minimizing the bias introduced if the internal standard is naturally present in the sample (i.e., the signal intensity contributed from naturally occurring internal standard element in the sample is insignificant).

The typical concentration of the internal standard solution contains 200 µg /L lithium6 and 100 µg/L of gallium, holmium, indium, rhodium, scandium, terbium, and yttrium.

The typical final concentration of the internal standard solution after mixing with the sample is approximately one-fifth the initial concentration of the internal standard solution.

8.2.2 Initial Calibration

Perform an initial calibration daily or for every analytical batch, whichever is more frequent. For routine analysis and higher level direct analysis, analyze a minimum of three routine standards (Section 7.3.2) and a CB (Section 7.3.4) according to Section 8.3.2. For low-level, direct analysis, analyze a minimum of three low-level standards and a CB. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV, CB, and SCV according to Section 8.3.2 immediately after analyzing the initial calibration standards. Use the appropriate levels for routine or low-level analysis. If QC criteria are not met, take corrective action as described in Section 9.2 and Appendix C.

8.2.3 Continuing Calibration

Prepare the CCV (appropriate for routine or low-level analysis) and CB as described in Sections 7.3.3 and 7.3.4 and analyze according to Section 8.3.2. Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Digest samples with turbidity >1 NTU and/or where silver is requested following EPA Region 9 Laboratory SOP 403 prior to analysis. For fish tissue, digest tissue samples following EPA Region 9 Laboratory SOP 420.

8.3.1.1 Aqueous Samples, Total Recoverable Analytes

For the determination of total recoverable analytes in water, digest samples following Region 9 Laboratory SOP 403 prior to analysis.

The digestion procedures used in SOP 403 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains <0.1mg/L silver.

8.3.1.2 Aqueous Samples, Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, add a 30 mL aliquot of the filtered, acid preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

For LCS and MS/MSD analyses, spike the samples at 25 µg/L for all analytes.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.3 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis

Drinking water samples with turbidity <1 NTU must be acidified and analyzed directly without digestion. Add a 30 mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

For LCS and MS/MSD analyses, spike the samples at 25 µg/L for all analytes.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in EPA Region 9 Laboratory SOP 403 prior to analysis.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined by direct analysis. For this reason, samples for silver analysis should be digested.

8.3.1.4 Fish Tissue Samples

Dilute the fish tissue digestate times four prior to analysis with DI water. The sample is now ready for analysis.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the sequence log or the LIMS sequence page, if available.

Make appropriate dilutions on the basis of screening data, sample history, or other information. Samples for routine analysis are diluted two times using the autodiluter or manual dilution. Samples for low-level analysis are run without dilution.

1. Enter autosampler loading list into the data system, to include initial calibration, all required QC, and samples. If autodiluter is to be used, set-up the QLS, MB, LCS, and samples and specify autodiluter locations. For initial routine analysis, set the autodiluter for two times dilution.

2. Load the samples to be analyzed in the autosampler according to their

designated positions in the loading list. The following table shows a typical analytical sequence:

Seq.	Description	Seq.	Description	Seq.	Description
1	CB	15	S2	29	S12
2	Cal Std 1	16	S3	30	CCV
3	Cal Std 2	17	S4	31	CB
4	Cal Std 3	18	CCV	32	S13
5	Cal Std 4	19	CB	33	S14
6	ICV	20	S5	34	S15
7	CB	21	S6	35	S16
8	SCV	22	S7	36	S17
9	QLS	23	S8	37	S18
10	MB	24	S9	38	S19
11	LCS	25	S10	39	S20
12	S1	26	S11	40	CCV
13	S1-MS	27	S11-MS	41	CB
14	S1-MSD	28	S11-MSD	42	QLS*

NOTE: *Analyze QLS if more than 40 analytical samples are to be analyzed.

3. Start the autosampler analytical sequence and collect results.

4. Review the results for QC compliance and off-scale results. Identify samples that must be re-analyzed in a different analytical run. Samples having analytes at concentrations higher than the highest calibration must be diluted into range and re-analyzed.

5. Compare all analyte results generated in DRC mode with the run in standard mode. If results from the two modes differ significantly, interference may be present. If interference is suspected, dilute and reanalyze in both modes.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should be given to both primary

and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes. Check additional monitored masses (i.e. krypton, bromine, palladium) as indicators of potential interferences (refer to Appendix D).

8.3.3.2 After set-up and calibration the instrument reports results for the analyzed solution in the units of µg/L. The instrument calculations include elemental correction calculations, internal standard correction calculations, and calibration factors.

8.3.3.3 Report results in µg/L using the following equation:

$$C = M \times \frac{V_f}{V_i} \times D$$

Where

C = final reported concentration, in µg/L
M = measured concentration reported by instrument, in µg/L
V_f = final volume of sample solution after sample preparation, in mL
V_i = initial volume of sample used in sample preparation, in mL
D = Sample analysis dilution factor, to account for any dilution performed after sample preparation. For samples analyzed by the direct analysis, include the factor introduced by the addition of 1:1 nitric acid.

8.3.4 Data and QC Review

- Review the results of instrument QC (ICV, CCV, CB, SCV, and QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

- Review the results of batch QC (MB, LCS, MS/MSD) immediately after their analysis to verify that the results are with QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

- Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

- The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

8.4 Maintenance

Perform maintenance if the tune standard does not pass. Observe for measured mass parameter at ±0.1 amu. Observe for resolution parameter of peak width at 0.65 ±0.025. Adjust DAC parameters, if necessary.

If daily performance is unacceptable, check sample introduction (pump tubing, torch, nebulizer, cones, etc.) for wear and cleanliness. Clean or replace as necessary. If daily performance is still unacceptable, perform Optimizations procedure as described in Elan Software Guide.

Refer to Appendix F for preventative maintenance operations and schedules.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

9.2.1 Initial Calibration

An initial calibration is performed daily or for each batch of analysis using a blank and a minimum of three calibration standards. A linear calibration forced through zero is used for calculation. Refer to Appendix C for

acceptance criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV, CB, and SCV. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including re-analysis or re-preparation and reanalysis of the initial calibration if necessary. The analysis may also continue but samples cannot be analyzed for the out-of-control analytes.

9.2.2 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standard. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one per 10 analytical samples and at the end of the analytical run. The recovery of analytes in the ICV and CCV are calculated as follows:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard
M	=	measured concentration of the analyte, µg/L
T	=	true concentration of the analyte in the ICV/CCV, µg/L

The ICV recovery criteria are listed in Appendix C. If the %R for any analyte in the ICV falls outside of the QC criteria, the instrument must be re-calibrated for at least the out-of-control analytes. Samples cannot be analyzed for the out-of-control analytes until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for any analyte in the CCV falls outside of the QC criteria, the instrument must be re-calibrated for at least the out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control CCV must be re-analyzed for the affected analytes.

9.2.3 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. The instrument must be re-calibrated at least for the out-of-control analyte and all samples not bracketed by acceptable CB results must be re-analyzed.

9.2.4 Second Source Calibration Verification

Analyze a SCV daily to verify the calibration standards and acceptable instrument performance. If the measured concentrations are not within ±10% of the true values, the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

The recovery of analytes in the SCV is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard
M	=	measured concentration of the analyte, µg/L
T	=	true concentration of the analyte in the SCV, µg/L

9.2.5 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after each 40 analytical samples. If using an autodiluter to analyze samples, use the diluter also to analyze the QLS. The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100xD$$

Where

%R	=	percent recovery of the standard
M	=	measured concentration of the analyte, µg/L
T	=	true concentration of the analyte in the QLS, µg/L
D	=	sample analysis dilution factor, to account for any dilution performed after sample preparation

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and re-analyze the QLS.

9.3 Batch QC

9.3.1 Method Blank

Analyze at least one MB with each batch of 20 or fewer field samples of the same matrix. MB values ≥½ the QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared, re-analyzed, and flagged as estimated:

- If the MB analyte value is ≥½ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and re-analyzed. The associated sample results can also be reported but will be qualified as estimated "J".

- If the MB analyte value is ≥½ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer samples of the same matrix. Recovery of analytes in the LCS is calculated as:

$$\%R = \frac{M}{T} \times 100xD$$

Where

%R	=	percent recovery of the standard
M	=	measured concentration of the analyte, µg/L
T	=	true concentration of the analyte in the LCS, µg/L
D	=	sample analysis dilution factor, to account for any dilution performed after sample preparation

If the recovery of the LCS does not meet the recovery criteria in Appendix C, re-analyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out- of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be re-prepared and re-analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 10 field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analytes of interest prior to any sample preparation. The spiking level must be the same as that used for the LCS.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$ = percent recovery
C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions
C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions
s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where

RPD = relative percent difference
C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions
C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the value of C is less than four times the value of s, apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s, $\%R$ is not calculated. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Sample QC

Internal Standard Response – Monitor the signal intensity for the internal standard masses throughout the analytical run. This information is useful in detecting instrument drift, sensitivity shift; dissolved solids content, and inherent internal standard (i.e., a natural constituent in a sample). The absolute intensity of any one internal standard must not deviate more than 60 - 125% from its original intensity in the calibration blank. If deviations greater than these are observed, examine the internal standard intensities with the following actions:

- If the intensities of the internal standards for the ICV, CCV, or CB are out-of-control, recalibrate and re-analyze the analytes affected by the out-of-control internal standards in the affected samples.

- If the intensities of the internal standards for the ICV, CCV, and CB are within control limits but sample internal standards are out-of-control, rerun the sample or rerun at an appropriate dilution for the analytes affected by the out-of-control internal standard.

- Report results from the original, undiluted, or least diluted sample where the internal standards are within the acceptance limits.

9.5 Method Performance

The following table summarizes method performance by matrix for the period October 2010 to December 2011.

Method Performance

Analyte	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Aluminum (Al)	LCS	21	104	91.6 - 116
Antimony (Sb)	LCS	36	102	98.2 - 106
Arsenic (As)	LCS	27	95	87 - 103
Barium (Ba)	LCS	24	102	94.3 - 109
Beryllium (Be)	LCS	19	98.9	85.5 - 112
Cadmium (Cd)	LCS	35	101	96.9 - 105
Chromium (Cr)	LCS	31	100	94.7 - 106
Cobalt (Co)	LCS	21	102	95.8 - 109
Copper (Cu)	LCS	35	103	96.2 - 109
Lead (Pb)	LCS	34	103	97.5 - 109

Analyte	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Manganese (Mn)	LCS	31	101	93.6 - 109
Molybdenum (Mo)	LCS	31	102	97.9 - 107
Nickel (Ni)	LCS	30	101	97 - 105
Selenium (Se)	LCS	37	101	94.7 - 107
Silver (Ag)	LCS	37	101	92.9 - 110
Thallium (Tl)	LCS	35	101	97.3 - 105
Thorium (Th)	LCS			
Uranium (U)	LCS	4	102	98.1 - 106
Vanadium (V)	LCS	24	99.7	93.4 - 106
Zinc (Zn)	LCS	36	102	95.2 - 109

The primary sources of analytical error are:

- Analytical balance
- Instrument calibration
- Pipette calibration
- Vial contamination

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used in this SOP in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the sequence log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides decision tree for reporting metals. Appendix H provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Laboratory QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Laboratory QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix I.

11 REFERENCES

USEPA Region 9 Laboratory. *Business Plan.*

USEPA Region 9 Laboratory. *Chemical Hygiene Plan.*

USEPA Region 9 Laboratory. *Environmental Management System.*

USEPA Region 9 Laboratory SOP 110, *Sample Receiving and Login.*

USEPA Region 9 Laboratory SOP 125, *Sample Disposal.*

USEPA Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures.*

USEPA Region 9 Laboratory SOP 403, *Aqueous Sample Preparation for ICP-AES and ICP-MS.*

USEPA Region 9 Laboratory SOP 420, *Microwave Digestion of Solid Samples.*

USEPA Region 9 Laboratory SOP 462, *Analysis of Total Suspended Solids By EPA Method 160.2.*

USEPA Region 9 Laboratory SOP 706, *Laboratory Waste Management Procedure.*

USEPA Region 9 Laboratory SOP 820, *Laboratory Discrepancy and Corrective Action Procedures.*

USEPA Region 9 Laboratory SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level.*

USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

USEPA Region 9 Laboratory SOP 880, *Demonstration of Capability.*

Perkin Elmer, *ELAN 6100 DRC Software Kit and Elan 6100 DRC Hardware Guide.*

U.S. Environmental Protection Agency Method 200.8, *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC Version, May 1994.*

U.S. Environmental Protection Agency SW846 Method 6020, *Inductively Coupled Plasma-Mass Spectrometry, Revision 1, January 1998.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP does not include mercury as an analyte. Mercury is listed as an analyte in the reference method.

2. The MS/MSD and LCS are spiked at 40 µg/L for selenium; the referenced method specifies 200 to 500 µg/L.

3. This SOP specifies analysis of a MSD for precision; the reference method specifies analysis of a laboratory duplicate.

4. A linear dynamic range (LDR) standard is specified in the reference method but not specified in this SOP. The EPA Region 9 Laboratory requires any sample with a concentration above the highest calibration standard be diluted and reanalyzed.

5. This SOP includes gallium for internal standard based on the manufacture's recommendation. Gallium is not listed as an internal standard in the reference method.

6. This SOP specifies that the MB acceptance criterion is less than one-half the QL. The reference method specifies no greater than 2.2 times MDL.

7. The antimony, indium, and molybdenum elemental equations used for calculations are taken from the instrument software and differ slightly from those specified in the reference method.

8. The SOP specifies that arsenic results be reported from arsenic oxide (AsO mass 91) using the Dynamic Reaction Cell (DRC) mode and not arsenic at mass 75 as the reference method specifies.

9. The SOP specifies that thallium results be reported from thallium 203 and not thallium 205 as the reference specifies.

10. The SOP specifies that cadmium results be reported from cadmium 114 and not cadmium 111.

11. This SOP extends the scope of analysis to include fish tissue.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analyte list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	QL, Routine Analysis, Water, µg/L	QL, Low-Level Analysis, Water, µg/L
Aluminum (Al)	7429-90-5	20	10
Antimony (Sb)	7440-36-0	0.5	0.25
Arsenic (As)	7440-38-2	0.5	0.25
Barium (Ba)	7440-39-3	1	0.5
Beryllium (Be)	7440-41-7	0.5	0.25
Cadmium (Cd111)*	7440-43-9	0.4	0.2
Cadmium (Cd114)	7440-43-9	0.4	0.2
Chromium (Cr)	7440-47-3	1	0.5
Cobalt (Co)	7440-48-4	0.25	0.125
Copper (Cu)	7440-50-8	2	1
Lead (Pb)	7439-92-1	1	0.5
Manganese (Mn)	7439-96-5	2	1
Molybdenum (Mo)	7439-98-7	0.5	0.25
Nickel (Ni)	7440-02-0	1	0.5
Selenium (Se78)**	7782-49-2	2	1
Selenium (Se82)	7782-49-2	1	0.5
Silver (Ag)	7440-22-4	0.25	0.125
Thallium (Tl)	7440-28-0	1	0.5
Thorium (Th)	7440-29-1	1	0.5
Uranium (U)	7440-61-1	0.25	0.125
Vanadium (V)	7440-62-2	4	2
Zinc (Zn)	7440-66-6	5	2.5

*Cd at mass 111 is only reported when interference or poor performance is detected in concentration that interferes with Cd at mass 114.

**Se at mass 78 is only reported when bromine is detected in concentration that interferes with Se at mass 82.

The following table provides the target analyte list for Fish Tissue with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	QL, Fish Tissue, mg/Kg
Aluminum (Al)	7429-90-5	8
Arsenic (As)	7440-38-2	0.2
Cadmium (Cd)	7440-43-9	0.2
Chromium (Cr)	7440-47-3	0.5
Copper (Cu)	7440-50-8	0.5
Lead (Pb)	7439-92-1	0.2
Nickel (Ni)	7440-02-0	0.4
Selenium(Se)	7782-49-2	0.4
Zinc (Zn)	7440-66-6	5

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
Correlation Coefficient	Each ICAL	≥ 0.995
ICV	After ICAL	90 - 110%
CCV	Every 10 Samples	90 - 110%
CB	After each ICV/CCV	<½ QL
SCV	After ICAL	90 - 110%
QLS	After ICAL & after every 40 analytical samples	60 - 140%
MB	Each Batch	<½ QL
LCS	Each Batch	85 - 115%
MS/MSD, Accuracy	Every 10 samples	70 - 130%
MS/MSD, Precision	Every 10 samples	≤20 RPD
Internal Standard	Every analysis	60 - 125% of initial CB

Instrument Sensitivity and Stability Check:

- For daily performance check, the RSD for each element must be <5%.
- Sensitivity should be, at a minimum, Mg - 6,000 CPS, In – 30,000 CPS, and U – 20,000 CPS.
- Oxide (Ce) and ++ (Ba) levels, approximately 3% or lower are preferred.

APPENDIX D.
INTERNAL STANDARD TABLES, ELEMENT ISOTOPE, & EQUATION

Table 1. Internal Standards and Limitations of Use

Internal Standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Gallium	71	c

NOTES:
Internal standards recommended for use with this method are shown in underlined text.
Internal standards typically used by the Region 9 Laboratory are shown in **bold** text.

a May be present in environmental samples.
b In some instruments, Yttrium may form measurable amounts of YO^{+} (105 amu) and YOH^{+} (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.
c Gallium is recommended by the manufacturer of the Elan DRC instrument being used at the EPA Region 9 Laboratory.

Table 2. Element Equations for Data Calculations - Standard Mode

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{123}C) - (0.127189)(^{125}C)$	1
As	$1.000(^{75}C) - (3.127)[(^{77}C) - (0.815)(^{82}C)]$	2
Ba	$1.000(^{137}C)$	
Be	$1.000(^{9}C)$	
Cd111	$1.000(^{111}C) - (1.073)[(^{108}C) - (0.712)(^{106}C)]$	3
Cd114	$1.000(^{114}C) - 0.026826(^{118}C)$	4
Cr	$1.000(^{52}C)$	5
Co	$1.000(^{59}C)$	
Cu63	$1.000(^{63}C)$	
Cu65	$1.000(^{65}C)$	6
Pb	$1.000(^{206}C) + 1.000(^{207}C) + 1.000(^{208}C)$	7
Mn	$1.000(^{55}C)$	
Mo	$1.000(^{98}C) - 0.11058(^{101}C)$	8
Ni60	$1.000(^{60}C)$	
Ni62	$1.000(^{62}C)$	9
Se78	$1.000(^{78}C) - 0.1869(^{76}C)$	10
Se82	$1.000(^{82}C)$	11
Ag	$1.000(^{107}C)$	
Tl	$1.000(^{203}C)$	
Th	$1.000(^{232}C)$	
U	$1.000(^{238}C)$	
V	$1.000(^{51}C) - (3.127)[(^{53}C) - (0.113)(^{52}C)]$	12
Zn	$1.000(^{66}C)$	
Ga	$1.000(^{71}C)$	
Ho	$1.000(^{165}C)$	
In	$1.000(^{115}C) - 0.014032(^{118}C)$	13
Li^6	$1.000(^{6}C)$	

Element	Elemental Equation	Note
Rh	$1.000(^{103}C)$	
Sc	$1.000(^{45}C)$	
Tb	$1.000(^{159}C)$	
Y	$1.000(^{89}C)$	

NOTES:

C Calibration blank subtracted counts at specified mass.

1 Isobaric correction for Te

2 Isobaric correction for ArCl, Se

3 Correction for MoO. Isobaric mass 106 must be from Cd only, not ZrO. An additional isobaric elemental correction should be made if palladium is present.

4 Isobaric correction for Sn. Used as primary mass for reporting.

5 The background for ClOH will normally be small and can be estimated from the reagent blank.

6 Used as alternate mass when ArNa interference apparent at Cu63.

7 Allowance for isobaric variability of lead isotopes

8 Isobaric elemental correction for Ru

9 Used as alternate mass when CaO and CaOH interferences at Ni60.

10 Used as alternate mass when HBr interference apparent at Se82, Isobaric correction for Ar2 dimer.

11 Some Ar supplies contain Kr as an impurity. Se is corrected for ^{82}Kr by background subtraction.

12 Correction for chloride interference with adjustment for ^{53}Cr. ClO 51/53 ratio may be determined from the reagent blank. Isobaric mass 52 must be from Cr only, not ArC^{+}.

13 Isobaric correction for Sn

Table 3. Analytical Isotope and Additional Masses that are monitored

Element of Interest	Isotope
Aluminum	27
Antimony	121, 123
Arsenic	75
Barium	135, 137
Beryllium	9
Cadmium	106, 108, 111, 114
Chromium	52, 53
Cobalt	59
Copper	63, 65
Lead	206, 207, 208
Manganese	55
Molybdenum	95, 97, 98
Nickel	60, 62
Selenium	76, 77, 78, 82
Silver	107, 109
Thallium	203, 205
Thorium	232
Uranium	238
Vanadium	51
Zinc	66, 67, 68
Bromine	79, 81
Krypton	83
Palladium	105
Ruthenium	101
Tellurium	125
Tin	118

NOTE: Isotopes used for analytical determination are underlined.

Table 4. Analytical Isotopes For DRC Analysis

Element of Interest	Isotope
Arsenic as Arsenic Oxide	91
Chromium	52

NOTE: Isotopes used for analytical determination are underlined.

Table 5. Internal Standard Groups - Standard Mode

Element	Internal Standard Group	Internal Standard
Be	1	Sc
Al	1	
V	1	
Cr	1	
Mn	1	
Co	1	
Ni	1	
Cu	1	
Zn	2	Y
As	2	
Se	2	
Mo	3	In
Ag	3	
Cd	3	
Sb	3	
Ba	4	Tb
Tl	4	
Pb	4	
U	4	
Th	4	

Table 6. Internal Standards - DRC Mode

Element	Internal Standard Group	Internal Standard
Cr	5	Ga
As as AsO	5	Rh

APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

Nebulizer Gas Flow:	0.85 - 1.05 mL/min (~0.90 typical)
Auxiliary Gas Flow:	1.20 mL/min
Plasma gas Flow:	12.0 mL/min
ICP RF Power:	1,100 - 1,500 watts (1,350 typical)
Pulse Stage Voltage:	700 - 2,500 (increases with age of detector to meet sensitivity parameters)
Analog Stage Voltage:	1,300 - 2,500 (increases with age of detector to meet sensitivity parameters)
Argon Line Pressure:	51 psi ± 1

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the Elan ICP-MS

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	As needed	Fill with 2% $HN0_3$.
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
Cones	Daily Weekly	Inspect for sample residues. Wipe clean or replace with clean cone as needed. Remove and inspect condition of cones. Replace if needed.
Torch Tip	Daily	Check for sample residues. Replace with clean glassware if needed.
Argon Dewar	Daily	Check for sufficient amount and pressure. Order as needed.
Autodiluter	Daily	Rinse thoroughly with reagent water after each use.
Auto-sampler and Peristaltic Pump	Weekly	Wipe spills or residues.
Nebulizer Spray	Weekly	Check, unclog or replace if needed.
Glassware	Weekly	Inspect and clean if needed.
Glassware & Cone alignment	Weekly	Perform X-Y alignment, if needed.
Air filters	Monthly	Clean or replace as needed.
Chiller Coolant	Monthly	Check level and top off as needed.
Vacuum Oil	Monthly	Check level and color, replace with fresh one if needed.

APPENDIX G.
DECISION TREE FOR REPORTING METALS

Aluminum (Al)	x		xxx
Antimony (Sb)	x		
Arsenic (As)	x		
Barium (Ba)	x		xxx
Beryllium (Be)	x		xxx
Boron (B)		xx	
Cadmium (Cd)	x		
Calcium (Ca)		xx	
Chromium (Cr)	x		
Cobalt (Co)	x		xxx
Copper (Cu)	x		xxx
Iron (Fe)		xx	
Lead (Pb)	x		
Magnesium (Mg)		xx	
Manganese (Mn)	x		xxx
Molybdenum (Mo)	x		
Nickel (Ni)	x		xxx
Potassium (K)		xx	
Selenium (Se)	x		
Silica (SiO_2)		xx	
Silver (Ag)	x		
Sodium (Na)		xx	
Strontium (Sr)		xx	
Thallium (Tl)	x		
Thorium (Th)	x		
Tin (Sn)		xx	
Titanium (Ti)		xx	
Uranium (U)	x		
Vanadium (V)		xx	
Zinc (Zn)	x		xxx

Where:

x = reported by ICP-MS
xx = reported by ICP-AES
xxx = If all 200.7 QC passes and the concentration is above the 200.7 QL, an element may be reported from the 200.7 analysis.

APPENDIX H.
TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms
- EPA Review Form
- ESAT technical review guide
- Discrepancy Reports (if applicable)
- Work Order Memo (if applicable)
- Daily folder review forms or checklists
- Analysis matrix listing all analytical runs (for organics only)

Tracking Forms
- Work Order(s)
- COC(s)

Sample Preparation (for projects that require extraction or digestion)
- Bench Sheets (and copies of notebooks, where used)
- Sample cleanup data and records (e.g. GPC logs)
- Sample homogenization records (for solid/waste/tissue samples)
- Moisture data (when applicable)

[Analysis Method] Data (For each method where multiple methods in package)
- Bench sheet(s) where not used in Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, when only one analysis is reported, separate calibration and sample data as:
- Initial Calibration Data (sorted by instrument and then by date)
- Sample Data (sorted by instrument and then by date)

Miscellaneous Data
- Other data as applicable (e.g. conductivity for perchlorate)
- Canister certifications (for volatiles in air analysis)

Standard Records
- Standards records from LIMS (and certificates of analysis, if required)

APPENDIX I.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 507
Revision: 7, Effective: 02/01/12

DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-MS

Revision	Effective Date	Description
7	02/01/12	1. Updated format to current EPA Region 9 Laboratory requirements. 2. Updated procedure to follow current internal COC practices. 3. Removed reference to instrument runlog. 4. Lowered reporting limits for some analytes and updated corresponding QLS concentrations. 5. Internal standard for Be changed from Li^6 to Sc. 6. Added fish tissue analysis. 7. Change cadmium primary reporting mass from 111 to 114 8. Minor edits throughout.